SUPPLEMENTARY MATERIAL

CO-POLYMERIZATION STUDIES OF VINYL CHLORIDE AND VINYL ACETATE WITH ETHYLENE USING A METAL CATALYST

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Computational details:
B3LYP density functional theory, which includes non-local gradient corrections to the Slater local exchange functional[1] and some exact Hartree-Fock exchange. We use parameters[2] referred to as Becke 3 along with the Becke non-local gradient correction,[3] the Vosko-Wilk-Nusair exchange functional,[4] and the Lee-Yang-Parr local and non-local correlation functional.[5]
Jaguar program (v4.0)[6]
6-31G* basis set used, except for 6-31G on coordinating ligand atoms not directly connected to metal
Hay and Wadt core-valence 18-electron relativistic effective-core potential on Fe[7]
Spin-restricted singlet states *without* spatial symmetry constraints
All energies are reported as internal energies (ΔE) without zero point energy, finite temperature enthalpy, or entropy corrections.
All structures are geometry optimized, Thus the Hessian (second derivative matrix) was diagonalized to show that the minima have no negative eigenvalues while the transition state structures have exactly one negative Hessian eigenvalue. Searches for transition structures were guided by a quadratic synchronous transit method, employing both reactant and product geometries to aid in the search along a reaction coordinate.
Solvation effects use the Poisson-Boltzmann continuum model (PBF)[8,9,10] available within the Jaguar (v4.0) program. This uses the molecular surface for the boundary with the solvent and calculates both the energy and forces due to the reaction field in the solvent arising from the QM charges in the molecule.
Toluene was considered as the solvent (dielectric constant[11] of ε=2.4 and a probe radius[12] of 2.76Å)

GENERAL PROCEDURES
Transfer of transition metal catalyst, methylalumoxane, and monomer solutions were carried out in a dry nitrogen atmosphere using vacuum line or dry box techniques. All solvents used were HPLC grade (Aldrich) and were dried before using. Perdeuterated VC and VA was obtained from Cambridge Isotope Laboratories and used as received. Ethylene (Aeriform) was instrument grade and was passed through an oxygen scrubber prior to use. Methylalumoxane were obtained from Akzo Nobel. All other reagents were purchased from Strem and Aldrich Chemical Co. 2,6-bis[1-(2-methylphenylimino)-ethyl]pyridine iron (II) chloride **1** was synthesized according to literature procedures.
Proton and carbon NMR spectra were obtained on a 250 MHz Bruker spectrometer. Chemical shifts reported are internally referenced to tetramethylsilane. Deuterium NMR spectra were recorded on a 400 MHz Varian Unity Plus spectrometer in o-dichlorobenzene at 100°C. Chemical shifts reported are internally referenced to *o*-dichlorobenzene-d_4. Gas chromatography data were obtained from a HP-5890 Series II gas chromatograph equipped with a 30 m x 0.25 mm x 0.25 μm film thickness DB-1 capillary column with FID detector. The temperature program used : Initial Temperature 40 °C (isothermal for 5

(1) Slater, J. Quantum Theory of Molecules and Solids, Vol. 4: The Self Consistent Filed for Molecules and Solids; Mc-Graw-Hill: New York, 1974.
(2) Becke, A. *J. Chem. Phys.* **1993**, *98*, 5648.
(3) Becke, A. *Phys. Rev. A* **1988**, *38*, 3098.
(4) Vosko, S.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
(5) Lee, C.; Yang, W.; Parr, R. *Phys. Rev. B* **1988**, *37*, 785.
(6) *Jaguar v4.0*; Schrödinger, Inc.: Portland, OR, 2000.
(7) Hay, P.; Wadt, W. *J. Chem. Phys.* **1985**, *82*, 299.
(8) Tannor, D.; Marten, B.; Murphy, R.; Friesner, R.; Sitkoff, D.; Nicholls, A.; Ringnalda, M.; Goddard, W.; Honig, B. *J. Am. Chem. Soc.* **1994**, *116*, 11875.
(9) Marten, B.; Kim, K.; Cortis, C.; Friesner, R.; Murphy, R.; Ringnalda, M.; Sitkoff, D.; Honig, B. *J. Phys. Chem.* **1996**, *100*, 11775.
(10) Cortis, C.; Friesner, R. *J. Comput. Chem.* **1997**, *18*, 1570.
(11) Lide, D. *CRC Handbook of Chemistry and Physics*; 81st ed.; CRC Press: Boca Raton, FL, 2000-2001. Dielectric constant at 23°C was used.
(12) Probe radius r_{solv} is calculated from $r^3=(3m\Delta)/(4\pi\rho)$ $(10^{24}Å^3/cm^3)$, where m is the molecular mass obtained by dividing the molecular weight[27] in g/mol by Avogadro's number, Δ is the packing density (assumed to be 0.5 in lack of detailed knowledge of liquid structure), and ρ is the density in g/cm^3 at 20°C.

min.), 40 °C to 300 °C at 10 °C / min. (isothermal for 10 min.) Mass Spectra were recorded by injecting 1 µl of each sample using a LEAP autosampler into a Varian 3400 gas chromatograph (GC) interfaced to a Finnigan SSQ-7000 mass spectrometer (MS) using column: 60m x 0.25mm x 0.25µ DB-1. Temperatures: 40 °C (isothermal for 5 min.), 40 °C to 300 °C at 10 °C / min. (isothermal for 10 min.) Inj. = Trans = Source = 220°C, Column head pressure: 20 psig He, Split flow: 60 cc/min.

General Procedure for Ethylene oligomerizations. To a 45 mL Parr reactor equipped with a pressure transducer was added 5 mL of toluene, catalyst **1** (0.002 g, 4.2 x10^{-3} mmol) , and MAO (200 µL of a 2.25M solution). The Parr reactor was sealed and placed in an aluminum heating block at 50°C. A single addition of ethylene at 150 psig (0.4 g, 14 mmol) was introduced into the reactor via an evacuated manifold. After 1h the ethylene polymerizations were quenched by venting excess pressure and adding 10 mL of 1.2M HCl. The oligomers were then isolated as a toluene solution by separating off the aqueous layer .

Co-oligomerization of D_3-VCM and Et with 2,6-Bis[1-(2-methylphenylimino)-ethyl]pyridine iron (II) dichloride 1. To a 45 mL Parr reactor equipped with a pressure transducer was added 5 mL of toluene, complex 1 (0.002 g, 4.2 x10^{-3} mmol), and MAO (100 µL of a 2.25M solution). The reactor was sealed and then placed into an aluminum heating block at 50°C. D_3-VCM (0.1 g, 1.5 mmol) was introduced into the reactor via an evacuated manifold. After the pressure equilibrated, approximately 2 min., 150 psig (0.4 g, 14.3 mmol) of Et was introduced into the reactor via an evacuated manifold. After 1 hour the reaction was quenched by venting of excess pressure and the slow addition of 10 mL of 1.2 M HCl. The oligomers were then isolated as a toluene solution by separating off the aqueous layer.

Co-oligomerization of D_6-VA and Et with 2,6-Bis[1-(2-methylphenylimino)-ethyl]pyridine iron (II) dichloride 1. To a 45 mL Parr reactor equipped with a pressure transducer was added 5 mL of toluene, complex **1** (0. g, 2.03 x10^{-3} mmol), MAO (100 µL of a 2.25M solution) and D_6-VA (0.2 g, 2.03 x10^{-3} mmol). The reactor was sealed and then placed into an aluminum heating block at 50°C. was introduced into the reactor via an evacuated manifold. After the pressure equilibrated, approximately 2 min., 150 psig (0.4 g, 14.3 mmol) of ethylene was introduced into the reactor via an evacuated manifold. After 1 hour the reaction was quenched by venting of excess pressure and the slow addition of 10 mL of 1.2 M HCl. The oligomers were then isolated as a toluene solution by separating off the aqueous layer.

FIGURE 1 GC/MS CHROMATOGRAM OF D3VCM/TOLUENE REACTION

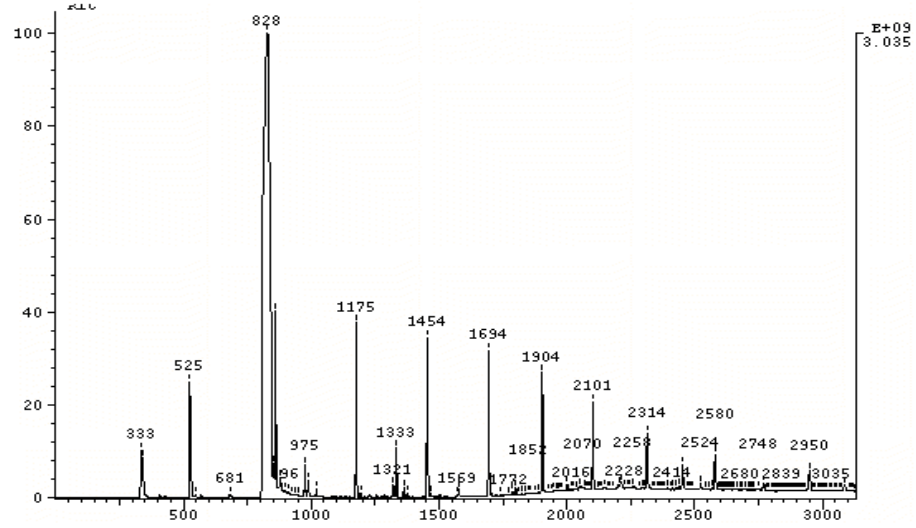

FIGURE 2 MASS SPECTRUM OF SCAN 525

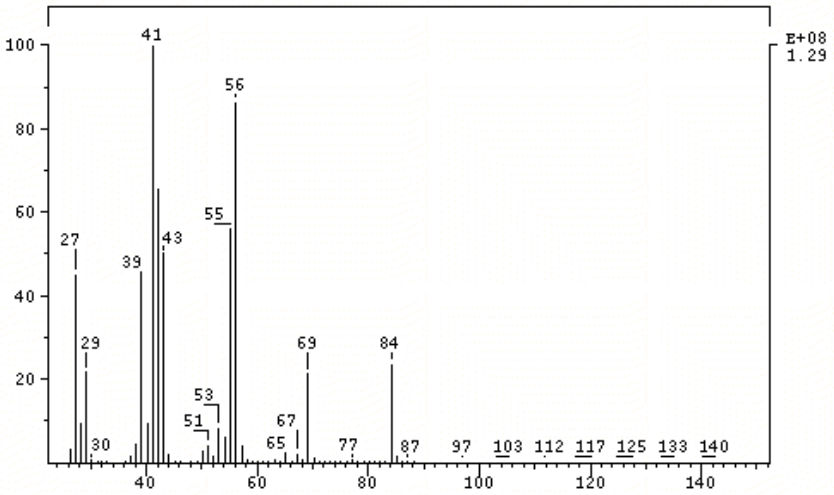

FIGURE 3 MASS SPECTRUM OF SCAN 522

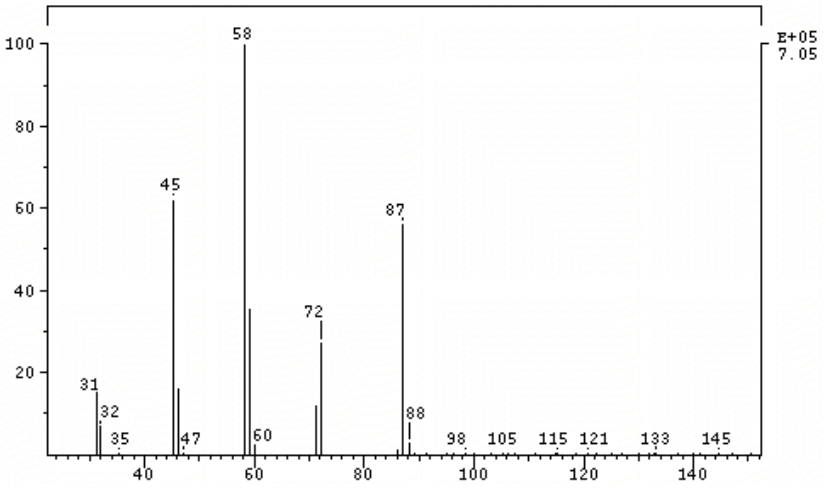

FIGURE 4 MASS SPECTRUM OF SCAN 861

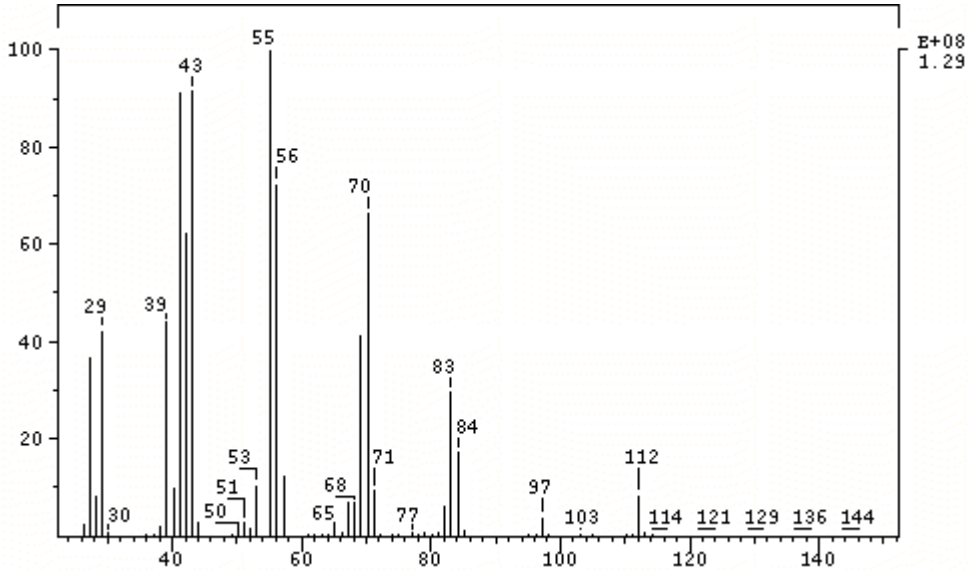

FIGURE 5 MASS SPECTRUM OF SCAN 858

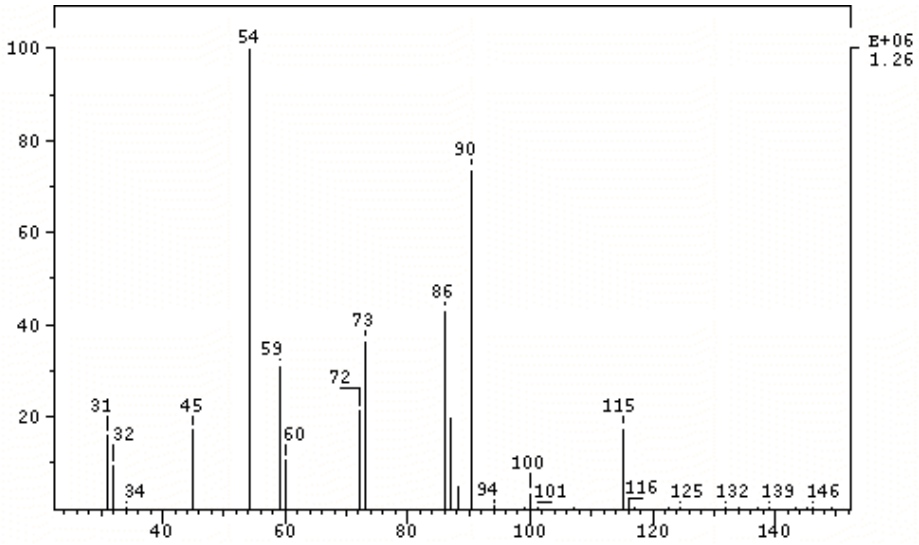

FIGURE 6 MASS SPECTRUM OF SCAN 1154

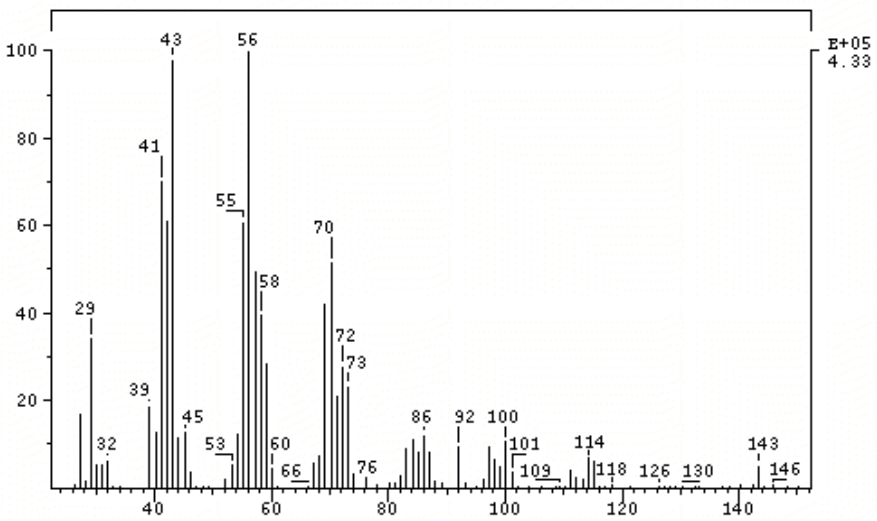

FIGURE 7. MASS SPECTRUM OF SCAN 1175

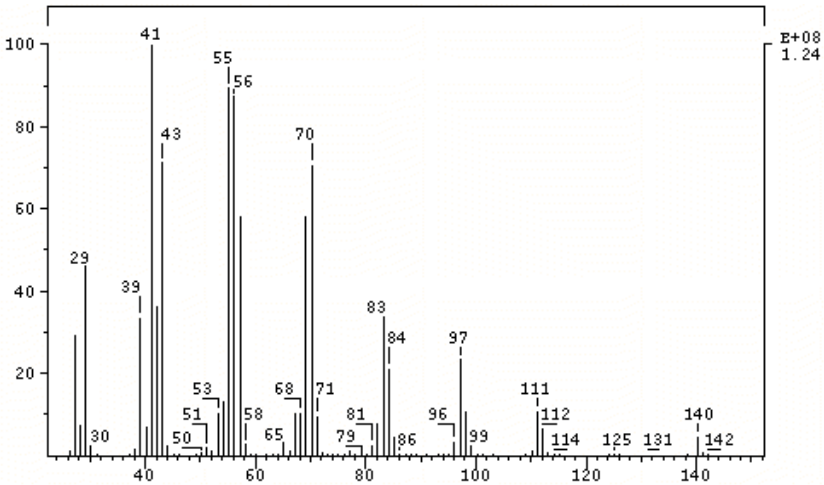

FIGURE 8. MASS SPECTRUM OF SCAN 1172

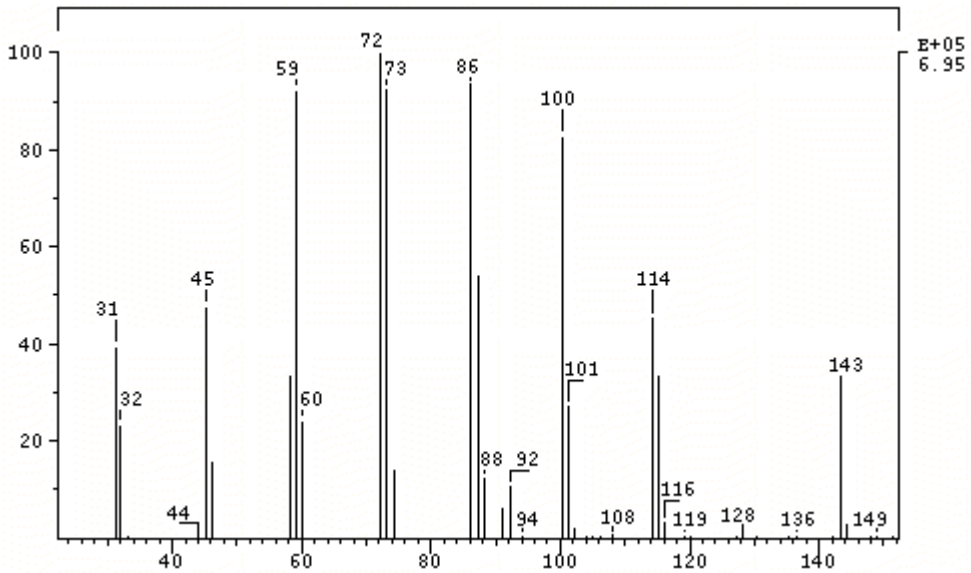

FIGURE 9. MASS SPECTRUM OF SCAN 1454

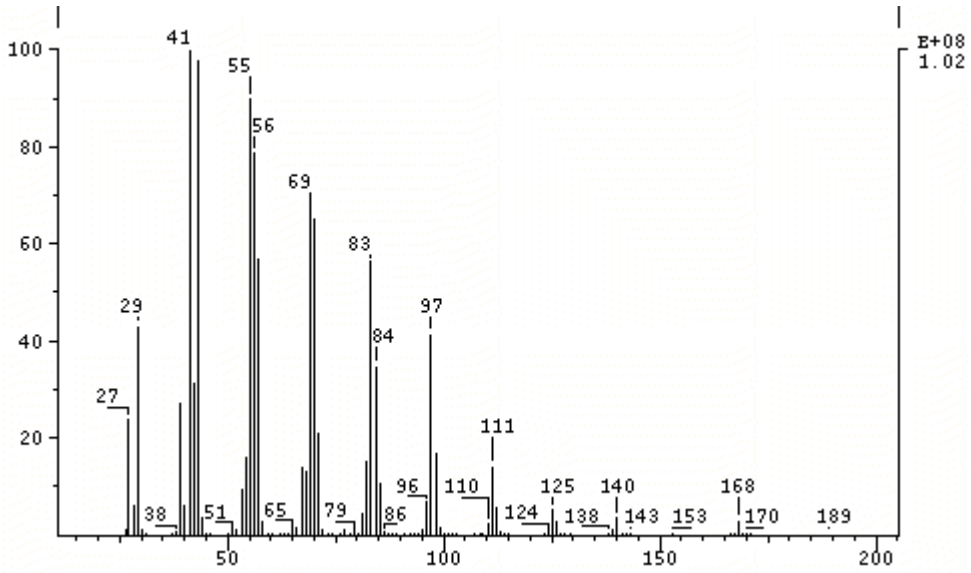

FIGURE 10. MASS SPECTRUM OF SCAN 1451

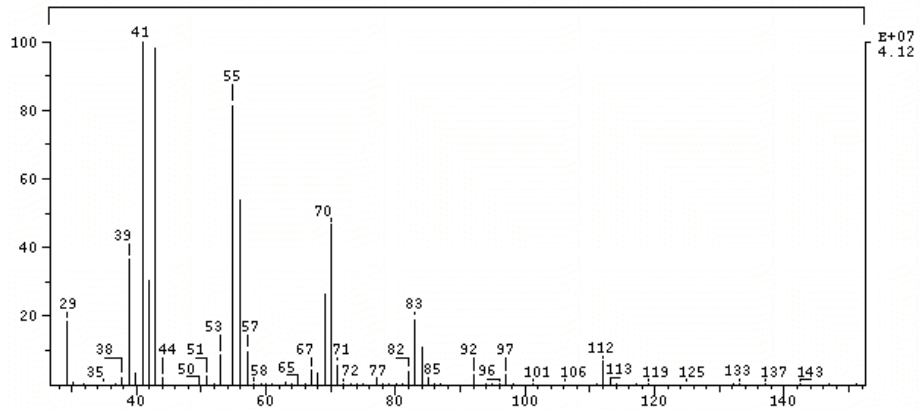

Figure 11. GC trace of oligomerization of Et and VA with complex **1**

Conditions : 40c-5min,10c/min-300c,20min

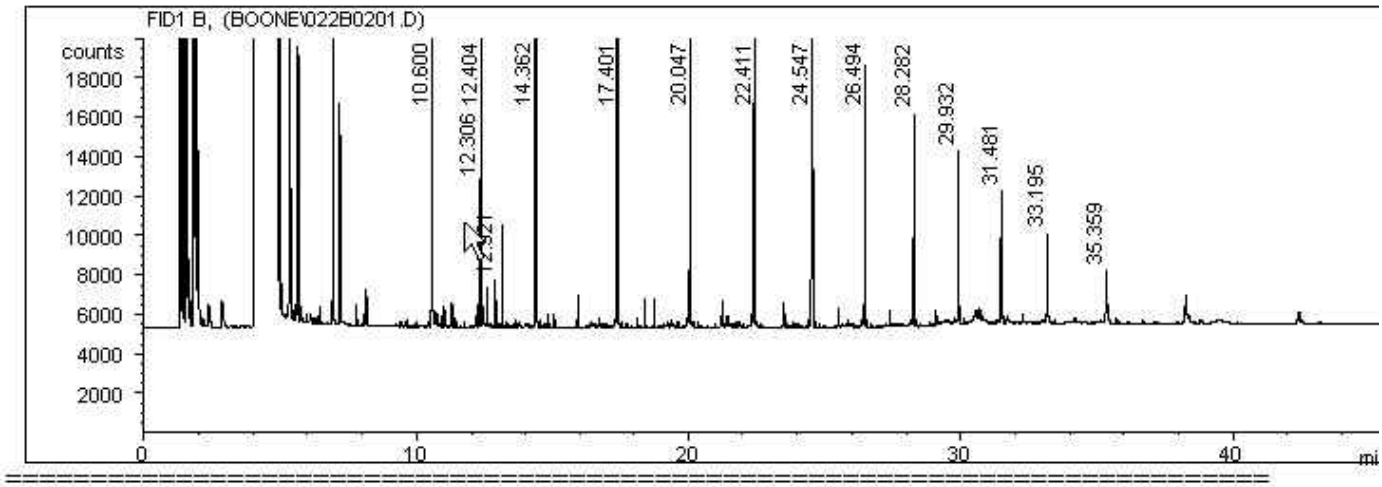

Figure 12. Mass Spectrum of deuterated C_8 fraction from VA/ET oligomerization

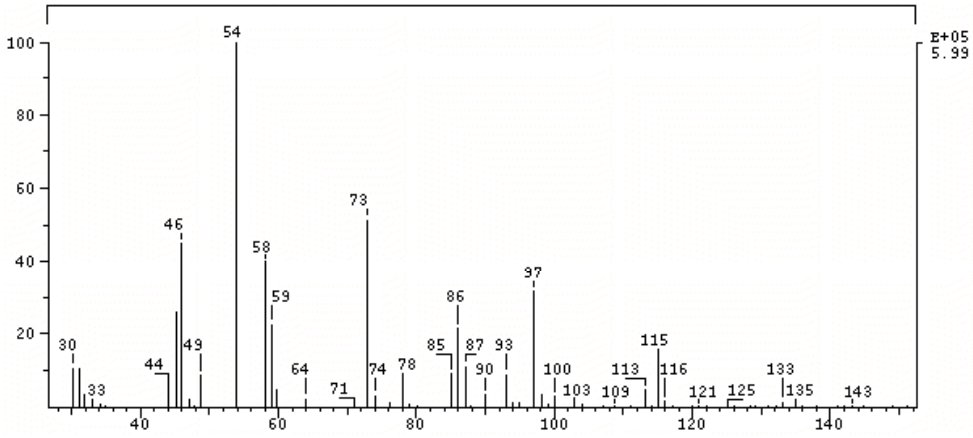

Figure 13. Mass Spectrum of C_8 fraction from VA/Et oligomerization

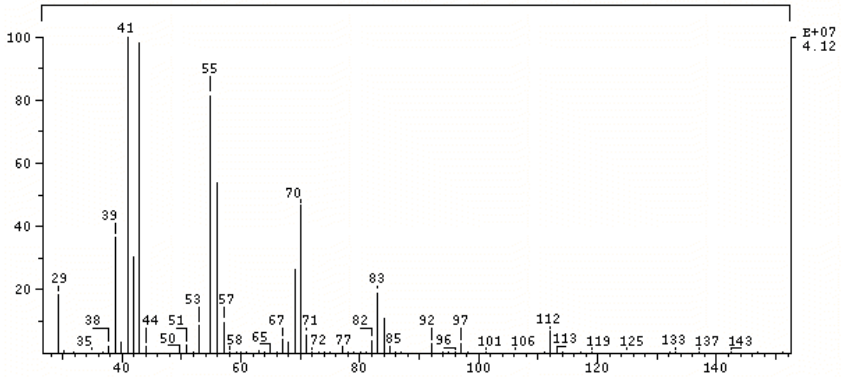

Figure 14. ^{13}C NMR Spectrum of oligomers from Et/ VC oligomerization in D_4-ODCB.

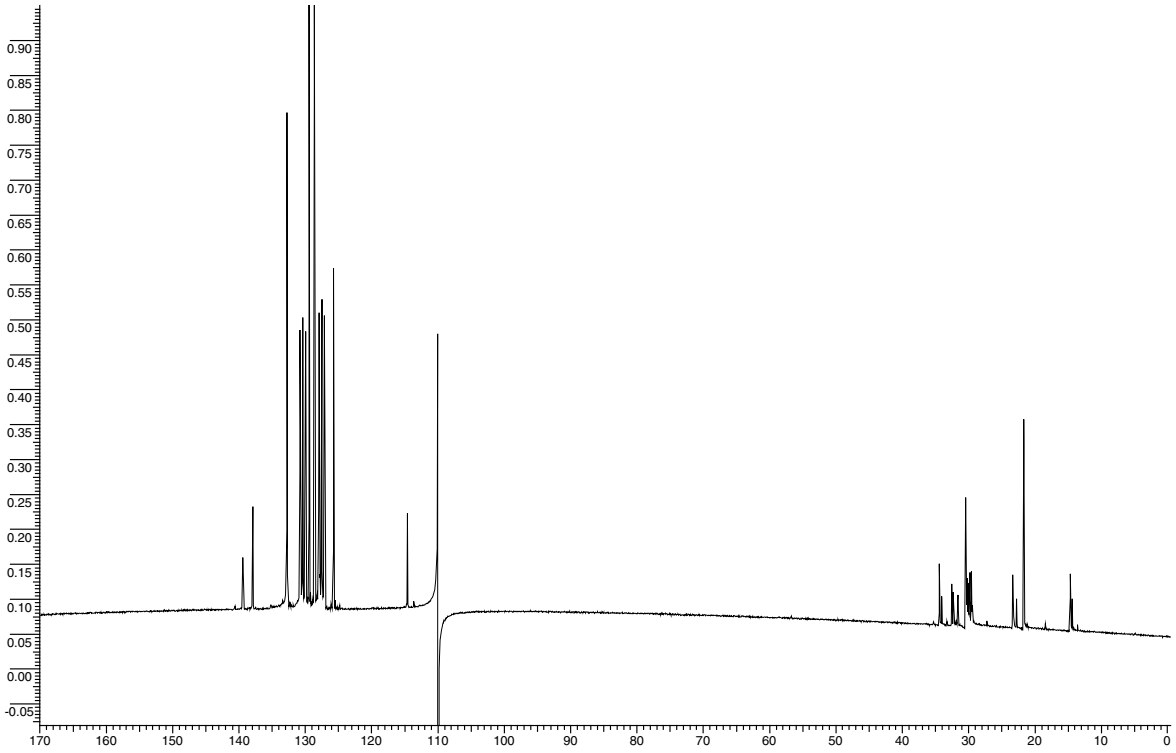

Figure 15. Expanded version of ^{13}C NMR Spectrum of oligomers from Et/ VC oligomerization in D_4-ODCB.

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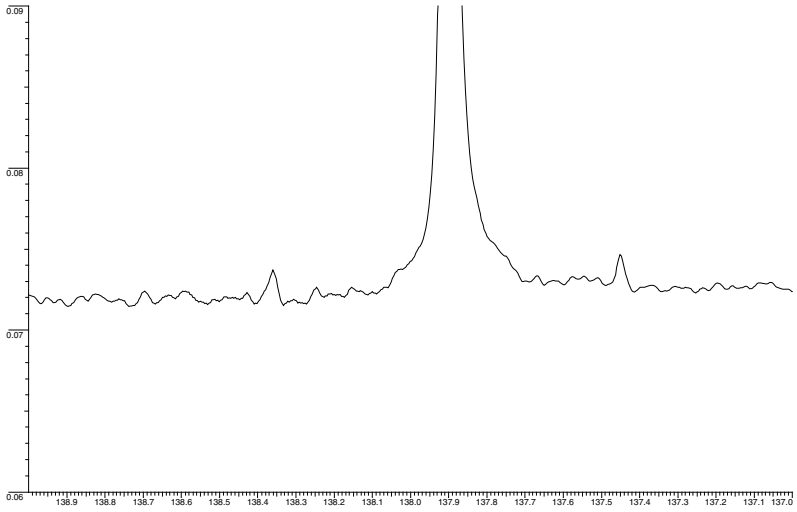

Figure 16. ^{2}H NMR Spectrum of oligomers from VA:Et oligomerization,

Note: alumoxane/ acetate residues were not removed from sample.